Special Properties Imparted to the 9-Phosphabicyclo[6.1.0]nonatriene System by a P-(2,4,6-tri-<u>t</u>-butylphenyl) Substituent; ¹⁷0 NMR Spectrum of a Bicyclic Phosphirane Oxide

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<u>Abstract</u>. 9-(2,4,6-Tri-t-butylphenyl)-9-phosphabicyclo[6.1.0]nona-2,4,6-triene gave an observable P-oxide with t-butyl hydroperoxide. Decomposition occurred by expulsion of the phosphorus fragment, possibly as ArP=0, rather than by the expected ring expansion to a phosphonin oxide. The ¹⁷O NMR shift of 18.0 is the most upfield known for a phosphine oxide.

We have previously reported¹ that oxidation of 9-phenyl- or $9-\underline{t}$ -butyl-9-phosphabicyclo-[6.1.0]nona-2,4,6-triene (<u>1</u>) with <u>t</u>-butyl hydrogen peroxide provided phosphonin oxides (<u>3</u>) as the first observable product. These compounds were not stable above room temperature and underwent intramolecular ring closure to give the <u>trans</u>-3a,7a-dihydrophosphindole system (<u>4</u>). The first step in the oxidation would appear to be the formation of the phosphirane oxide (<u>2</u>), but this species was not detectable because of the rapidity of cleavage of the C-C bond of its phosphirane unit.



Placing the 2,4,6-tri-<u>t</u>-butylphenyl substituent on phosphorus is a widely used and highly efficient method for the stabilization of especially reactive species, and it seemed likely that the oxidation and rearrangement products from the bicyclic phosphirane <u>1</u> might also be subject to this stabilization effect. Either product would be highly desirable in stabilized form, the former because only one other phosphirane oxide has ever been prepared,² the latter because no monocyclic phosphonin oxide is yet known to be stable at room temperature. Accordingly, we synthesized 9-(2,4,6-tri-<u>t</u>-butylphenyl)-9-phosphabicyclo[6.1.0]nona-2,4,6-triene (<u>5</u>) in the usual way³ by reacting dilithium cyclooctatetraenide with 2,4,6-tri-<u>t</u>-butylphenylphosphonous dichloride. The product was obtained in 86% yield as an air-stable, crystalline compound that was purified by silica gel chromatography with elution by hexane, m.p. 110-112°C. It was characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy.⁴



Phosphirane <u>5</u> was smoothly oxidized with <u>t</u>-butyl hydroperoxide in CHCl₃ at room temperature; the oxidation did not occur at the usual temperature¹ of -15°C. All <u>5</u> was consumed after standing overnight; the major ³¹P NMR signal appeared at δ -38.3 which was quite unlike that observed for the phosphonin oxides from related oxidations (δ +16 to +34). Since a negative shift has been reported for the only other known phosphirane oxide² (1,2,3-tri-<u>t</u>-butyl, δ -1.27), structure <u>6</u> was suggested for the oxidation product. Removal of volatiles at 0.05 mm Hg left a yellow oil that partly crystallized on standing. In the absence of air or water, it was unchanged after several weeks. Confirmation of structure <u>6</u> came from its ¹H and ¹³C NMR spectra.⁵ The symmetry of the product was evident from the latter, which contained only signals for ring sp² carbons and one sp³ carbon. The quite small value of ¹J_{PC} of the ring carbon (25.2 Hz) was also indicative of a phosphirane oxide.² Not a trace of the phosphonin oxide (<u>3</u>), nor of the dihydrophosphindole oxide (<u>4</u>), was detected. The tri-<u>t</u>-butyl substituent has therefore completely changed the chemistry of the bicyclic phosphirane system <u>1</u>, and has allowed the first instance of the formation of a stable P-oxide by direct oxidation of a phosphirane.⁶

The ¹⁷O NMR spectrum was also obtained on this compound. In other work in progress in this laboratory,⁷ it has been shown that the carbon framework of phosphines can have very strong effects on the 170 shift, with a range recorded so far of 39.6 to 116.4 ppm. This parameter is therefore of value in structure analysis. Compound 6 had a chemical shift of 18.0 ($H_2O = 0$), a value which is some 20 ppm upfield of others so far observed for a phosphine oxide. At first this result seemed surprising since in our other work we had shown that strained rings with 4 or 5 members had shifts very far downfield. However, on an empirical basis, this is just the effect to expect for a three-membered ring; we have found that there is a linear correlation between the 170 shift of a phosphine oxide and the 31P NMR shift of the corresponding phosphine (not the oxide). Since phosphiranes give the most upfield ³¹P NMR signals known for tertiary phosphines, this correlation would predict that the ¹⁷O shift would also be the most upfield, as indeed is observed. The correlation will be discussed in more detail elsewhere.⁸ The 17 O measurement on compound 6 therefore provides proof of a new nature that the phosphirane ring has been preserved in the oxidation. The ${}^1\mathrm{Jp}_{
m PO}$ value of 166 Hz also is in accord with the phosphoryl structure.⁷ This parameter, unlike the chemical shift, is relatively insensitive to structural changes and lies in the expected range.

In chloroform solution, phosphirane oxide <u>6</u> slowly decomposed (90% after 3 days). One product was identified as cyclooctatetraene from its characteristic ¹H NMR signal at δ 5.8. A phosphorus-containing product with ³¹P NMR δ +16.4 was also formed. This compound possessed a P-H bond as evidenced by a splitting of the ³¹P NMR signal by 604.5 Hz when ¹H coupling was

allowed. This compound is tentatively identified as an anhydride of 2,4,6-tri-<u>t</u>-butylphenylphosphinic acid (<u>8</u>). After standing for several additional days, such solutions developed ³¹P NMR signals at +14.7 and +24.7. The former may be that of a second diastereoisomer (<u>9</u>) of anhydride <u>8</u>; the latter had a P-H coupling constant of 576.2 Hz, and was identified as 2,4,6tri-<u>t</u>-butylphenylphosphinic acid (<u>10</u>, δ ³¹P +24.7, J_{PH} 580 Hz⁹). Addition of water caused hydrolysis of the anhydrides and all phosphorus terminated in the form of the phosphinic acid 10.



The decomposition products of phosphirane oxide <u>6</u> suggest a mechanism involving retrocycloaddition with the release of a phosphorus fragment such as <u>7</u> and cyclooctatetraene. The inevitable traces of water then react with <u>7</u> to form <u>8</u> and <u>9</u>. A similar retrocycloaddition was encountered by Quast and Heuschmann² with tri-<u>t</u>-butylphosphirane oxide, the only other known phosphirane oxide. A mechanism involving an initial addition of water to the P=O group, followed by retrocycloaddition, seems less likely because of the steric hindrance to such attack provided by the <u>t</u>-butyl substituents of <u>6</u>, and does not account for the formation of anhydrides. Species <u>7</u> is of considerable current interest and attempts to confirm its involvement by trapping experiments are part of another study now in progress.

Richter reported¹⁰ that the l-<u>t</u>-butyl derivative of bicyclic phosphirane <u>1</u> undergoes rearrangement thermally to provide a dihydrophosphindole as the observed product. It is probable, but not proved, that a phosphonin is an intermediate. With the larger tri-<u>t</u>-butylphenyl substituent on P in <u>5</u>, it seemed possible that such an intermediate, highly desired as a potentially $10-\pi$ electron and aromatic system, might be sufficiently stabilized to allow its detection. Phosphirane <u>5</u> was therefore subjected to heating at 65°C in toluene (7 hr.), conditions similar to Richter's. The compound was indeed completely rearranged, but the product had a far upfield ³¹P NMR shift (δ -67.0) and therefore is suggested from the work of Katz³ on the 1-phenyl analog (δ -79) to be <u>syn</u>-9-(2,4,6-tri-<u>t</u>-butylphenyl)-9-phenylbicyclo[4.2.1]nona-2,4,7triene (<u>11</u>), and not the phosphonin or the dihydrophosphindole from its ring closure. The product has not been further examined. Therefore in this reaction the presence of the <u>t</u>-butyl groups on the benzene ring has not introduced any special effect.



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- 5. NMR spectral data (Varian XL-300, CDCl₃ solution): ³¹P, δ -38.8; ¹H (partial) δ 1.27 (d, J_{PH} = 1.4 Hz, 9H, p-Me₃C), 1.60 (s, 18H, o-Me₃C), 2.04 (d, J_{PH} = 7.5 Hz, 2H, PCH), 7.67 (d of d, J = 5.5, J = 1.4 Hz, 2H, Ar-H); ¹³C, δ 27.7 (d, J = 25.2 Hz, C-2), δ 30.9 (s, C-11), 33.2 (s, C-13), 33.6 (d, J = 18.8 Hz, C-12), 39.0 (d, J = 17.7 Hz, C-10), 121.5 (d, J = 5.8 Hz, C-8), 123.8 (d, J = 14.1 Hz, C-3), 127.0 (s, C-5), 133.5 (d, J = 14.1 Hz, C-4), 153.0 (d, J = 5.0 Hz, C-9), 155.9 (d, J = 10.0 Hz, C-7) (C-6 not observed); ¹⁷O (CD₃CN, 50°C) δ +18.0 (J_{PO} = 166 Hz).
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